MAUL FOSTER ALONGI

MEMORANDUM

To:	Dana Bayuk	Date:	September 18, 2009
From:	James Peale, RG	Project:	8128.01.20
RE:	Revised REMChlor Modeling Parameters - Siltronic Corporation EIB Source Control		

As part of the enhanced *in situ* bioremediation (EIB) implementation work, MFA developed calibrated simulations of the fate and transport of TCE and its degradation products following implementation of EIB in the source area. Simulations were conducted with the EPA-developed REMChlor model. The objective of the modeling was to evaluate the potential for a "slug" of increased concentrations of degradation products (specifically, DCE isomers and vinyl chloride) in groundwater to travel downgradient from the injection zone. As noted in the June 30, 2009 Performance / Effectiveness Plan (PEP), the calibrated model did not predict this scenario.

A secondary outcome of the "slug" analysis was the prediction of remediation timeframes and inferred EIB performance. In their comments, DEQ noted that the model assesses source remediation and plume attenuation under conditions that simulate rapid source depletion. The following model parameters were identified by DEQ as potentially unrepresentative of site conditions: Darcy velocity, source concentration, source retardation, gamma, and contaminant biodegradation rates. In its comments, DEQ also suggested alternative values for these parameters.

Alternative versions of the model were developed using DEQ's suggested values for individual parameters while holding previously simulated inputs constant. Additionally, one model run using all DEQ suggested values was completed. TCE and daughter product concentrations were compared to calibration targets at Zones 1, 2, and 3 (Table 1). The calibration targets for Zones 1 and 2 are concentration ranges based upon data from pilot study monitoring wells WS-19-71/101 and WS-18-71/101 (respectively). The calibration targets for Zone 3 are concentration ranges based upon presumed baseline conditions from the January 2009 Group 3 performance monitoring well (PMW) sampling event. The time required to reach Joint Source Control Strategy (JSCS) Screening Level Values (SLVs) for each compound was also predicted (Table 2).

In order to test the REMChlor model's sensitivity to individual parameters, several additional alternative modeling runs were conducted and contaminant concentration responses to changing input values at critical locations[1] were plotted for the baseline (pre-injection) and two years post-injection. A discussion of the tested parameters and results follows.

[1] Critical locations to measure source persistence for TCE and DCE were zones 1 and 2. The critical location to measure daughter product yield and persistence was Zone 3 (i.e., Group 3 PMWs).

Source Concentration: In the initial model, the source concentration was (conservatively) set to 500,000 ug/L, based upon concentrations measured in direct-push reconnaissance sampling points. DEQ suggested that using this value overestimates mass flux out of the source areas, and could therefore underestimate source persistence. As per DEQ suggestion, the historical average TCE concentration at well WS-13-69 of 160,000 ug/L was used to create an alternative version of the model.

As a result of using this value, predicted plume tailing and source persistence increased. The lower concentration results in predicted Group 1 and 2 concentrations were inconsistent with observed results. The time to reach remediation targets in the Group 3 PMWs for TCE, DCE, and VC was increased to 12.5, 15 and 22 years, respectively. The sensitivity analyses for source concentration (Figures 1 and 2) indicate that increasing source concentration is positively correlated with increasing contaminant concentration at the baseline; however, two years after injection, Zone 1 and 2 contaminant concentrations generally show a negative correlation with increased source concentration. The latter result supports the DEQ suggestion that decreased source concentration reduces the possibility of overestimation of mass flux from the source area.

Retardation Factor and Darcy Velocity: Contaminant transport velocity through the saturated zone is described by the retardation factor, R and pore water (Darcy) velocity. The initial modeling used a retardation factor of 1.6, which is the average of typical values for TCE, DCE, and VC as well as average linear (aka seepage) velocities that averaged 0.625 ft/day. According to DEQ suggestions, a reasonably conservative value for the retardation factor was modeled on VC fate and transport parameters (R = 1.1, minimum velocity (vmin) =1, maximum velocity (vmax) =2).
A reduction in the retardation factor led to a decrease in the time to reach the remediation targets by a year compared to the initial model. Changing the Darcy velocity to the DEQ-suggested values did not significantly affect the time required to reach the remediation targets compared to the initial model, but calibration targets for TCE and DCE at injection plus two years were overshot for the Group 1 and 2 PMWs.

For the sensitivity analyses of the Retardation factor (Figures 3 and 4), the model was run with R values between 0.8 and 1.6. The model was not particularly sensitive to changing R, except that it overpredicts DCE in Zone 2 with the lower R values. Additionally, lower R values underpredict DCE and VC concentrations in Zone 3 two years after injection. A sensitivity study was not performed for vmin and vmax, since within the range of appropriate values for this input; the modeled results did not change significantly. However, using the DEQ-suggested Darcy velocity values resulted in predicted TCE and DCE concentrations at Zones 1 and 2 that were higher than those recorded at Group 1 and 2 monitoring wells. Application of the DEQ-suggested values for velocity did not impact calibration as much as using the DEQ-suggested values for source concentration.

Biodegradation Rates: The variation of contaminant concentration with time and distance is governed by the combined effects of sorption, dispersion, and biodegradation. In order to accurately represent biodegradation constants for TCE and its daughter products, it may be necessary to distinguish contaminant attenuation due to biodegradation from attenuation due to sorption and dispersion. DEQ indicated in its comments that the initial model assumptions do not address this distinction.

An alternative model was parameterized using biodegradation constants calculated using the method of Buscheck and Alcantar (1995)[1]. The resulting lambda values were: 2.85 yr^{-1}, 4.3 yr^{-1}, and 2.77 yr^{-1}. Resulting concentrations for TCE, DCE, and VC were significantly higher than Zone 3 PMW readings (except for DCE at baseline and TCE at two years after EIB injection). Zone 1 and 2 calibration targets were overshot for DCE and TCE at all times after injection. The resulting times to reach contaminant remediation targets were increased by two years over those calculated using the previous model.

Gamma: The gamma factor is used in the model to describe the partitioning of source mass and source concentration with time. Initially, the model was calibrated using a gamma of 0.725. In their comments, DEQ suggested that values of gamma less than one are representative of (a) contaminants distributed in high permeability source-area materials and/or (b) situations where source mass decreases at a greater rate than concentration (i.e., rapid source depletion). Condition (a) is not explicitly described in the REMChlor model, and the equation describing the relationship between mass removal, rate of concentration change, and gamma does not incorporate a term related to permeability. Consistent with DEQ's suggestion, values of gamma between one and two were applied in modeling runs. In an attempt to use gamma as a final calibration parameter, all previous DEQ-suggested inputs were used during the gamma-varying runs.

Additionally, the actual stoichiometric ratio of 0.74 was used in these models for the Yield ratio parameter. In the initial model, an artificial stoichiometry of 6:1 (TCE:DCE) was used for this input to better calibrate results to pilot study data. However, since the changes in the other parameters generally resulted in increases in daughter product concentrations, a yield factor of 0.74 better represented data gathered from Group 1 and 2 PMWs.

For a gamma value of 1.01, Zone 3 calibration targets were generally met for baseline (Figure 5). However, calibration targets for DCE and VC at two years after injection were not met, resulting in an aggressive prediction for the Group 3 PMWs (Figure 6). Additional increases in gamma do not greatly decrease contaminant concentrations. However, the time to meet SLVs was predicted for all gamma values tested, and it was found that increasing gamma by 0.5 linearly increases time to reach the VC remediation target by a factor of 3. This linear increase results in overly conservative remediation timeframes which are not useful for predicting performance or developing a performance monitoring program.

Regarding gamma, the REMChlor manual states the following:

> "An important characteristic of source zones with gamma greater than or equal to one, is that the source is never completely depleted and the source discharge is always greater than zero, even at large times…this happens because the rate of discharge from the source drops as fast or faster than the rate of mass depletion of the source. When gamma < 1, the source has a finite life, and the source discharge eventually is equal to zero."

[1] Buscheck, T.E., and C.M. Alcantar, 1995. "Regression Techniques and Analytical Solutions to Demonstrate Intrinsic Bioremediation." In, *Proceedings* of the 1995 Batelle International Conference on In-Situ and On Site Bioreclamation, R. E. Hinchee and R. F. Olfenbuttel eds., Batelle Memorial Institute, Butterworth-Heinemann, Boston, MA.

The pilot study data demonstrated that the TCE source discharge was effectively reduced to zero, as demonstrated by non-detect values of TCE and declining trends of the daughter product (cis-1,2-DCE). These data suggest that the TCE source in the pilot study injection zone was completely depleted. The pilot study data support use of a gamma value less than 1, where the decrease in mass occurs at a faster rate than the decrease in concentrations. It appears that the correct value of gamma for the model will require additional data for confirmation, and should be readjusted following incorporation of the source removal term.

Conclusion: The net impact of the suggestions that DEQ has made on the inputs for the Draft Plan REMChlor model is that TCE source persistence is increased (contrary to observed data), while downgradient concentrations of TCE and its daughter product attenuate at a much slower rate than previously predicted or observed during the pilot study. Calibration targets were not met as well as the initial modeling scenario.

Running the model with a gamma factor greater than 1 significantly decreases the attenuation rate of VC. The most significant driver for the increased time to reach SLVs is the decrease in source concentration to 160,000 ug/L from 500,000 ug/L. MFA acknowledges the effects of decreasing the source concentration, and recommends revisiting the source concentration term (at both the observed and DEQ-suggested levels) in the context of revised gamma values and incorporating the source removal variable (which was set aside in the initial model).

One result of adjusting the model using DEQ's suggestions is a more conservative assessment of the attenuation of TCE and its daughter products in the source area and plume. For most of the suggested adjustments, the calibration targets for TCE and DCE were generally not met in the two source area monitoring groups, with predicted concentrations of these compounds higher than observed during the pilot study or early implementation data. The adjusted REMChlor model is therefore likely to underestimate the performance of the EIB implementation, and may not be appropriate for predicting timeframes for remediation or implementing contingency actions. Based on the results of incorporating DEQ's suggestions, MFA recommends the following:

1) Developing a source removal rate based on Group 1 PMW data for use in the REMChlor model. The source removal term will be applied with an increased number of streamtubes to prevent a "sawtooth" output (the apparent "instability" noted in the June 30, 2009 submittal).

2) Adjusting the timestep of the model output to 0.25 years to better match the rapid depletion of TCE in the source area.

3) Revising calibration targets based upon the refined timestep and early performance data from all three PMW groups.

Table 1
Calibration Targets for Siltronic REMChlor Model
Siltronic Corporation
Portland, Oregon

Target concentration Ranges from Pilot Study Data (mg/L)

TCE

Injection + 2 yrs	0.1	0.1	0.5
Baseline	100-200	100-200	0.5
Distance from source (m)	1	5	125

DCE

Injection + 2 yrs	0.1	0.1	5
Injection + 0.5 yrs	200	200	5
Baseline	50	50	2-5
Distance from source (m)	1	5	125

VC

Injection + 2 yrs	0.1	45	2
Injection + 1 yrs	20-70	30-45	2
Baseline	0.05	0.05	1-2
Distance from Source (m)	1	5	125

Table 2
Change in Time to Reach SLVs Using DEQ Suggested Parameters
Siltronic Corporation
Portland, Oregon

Parameter changed	Time to reach SLVs in Zone 3 (yrs)		
	TCE	DCE	VC
None (initial model)	6.5	7.5	9
Source concentration (C_o) increased to 0.16 g/L from 0.5 g/L	12.5	15	22
R decreased to 1.1 from 1.6	5.5	7	8.5
vmin = 1, vmax = 2 (Previous: vmin = 0.5, vmax = 2.788)	6	7.5	9
Zone 3 biodegradation constants†	8	9	11
All above parameters adjusted	16	20	23
Gamma = 1.01‡	18.5	16.5	45
Gamma = 1.25‡	21	17	74

†Zone 3 biodegradation constants = 2.85, 4.3, 2.7 yr-1 for TCE, DCE, and VC, respectively (Previously: 4, 10, 11 yr-1 for TCE, DCE, and VC, respectively).

‡Parameters other than gamma are changed from the standard model to all other suggested DEQ parameters above (initial gamma = 0.725).

Figure 1
Sensitivity of Contaminant Concentrations to Changes in Source Concentration at Baseline
Siltronic Corporation
Portland, Oregon

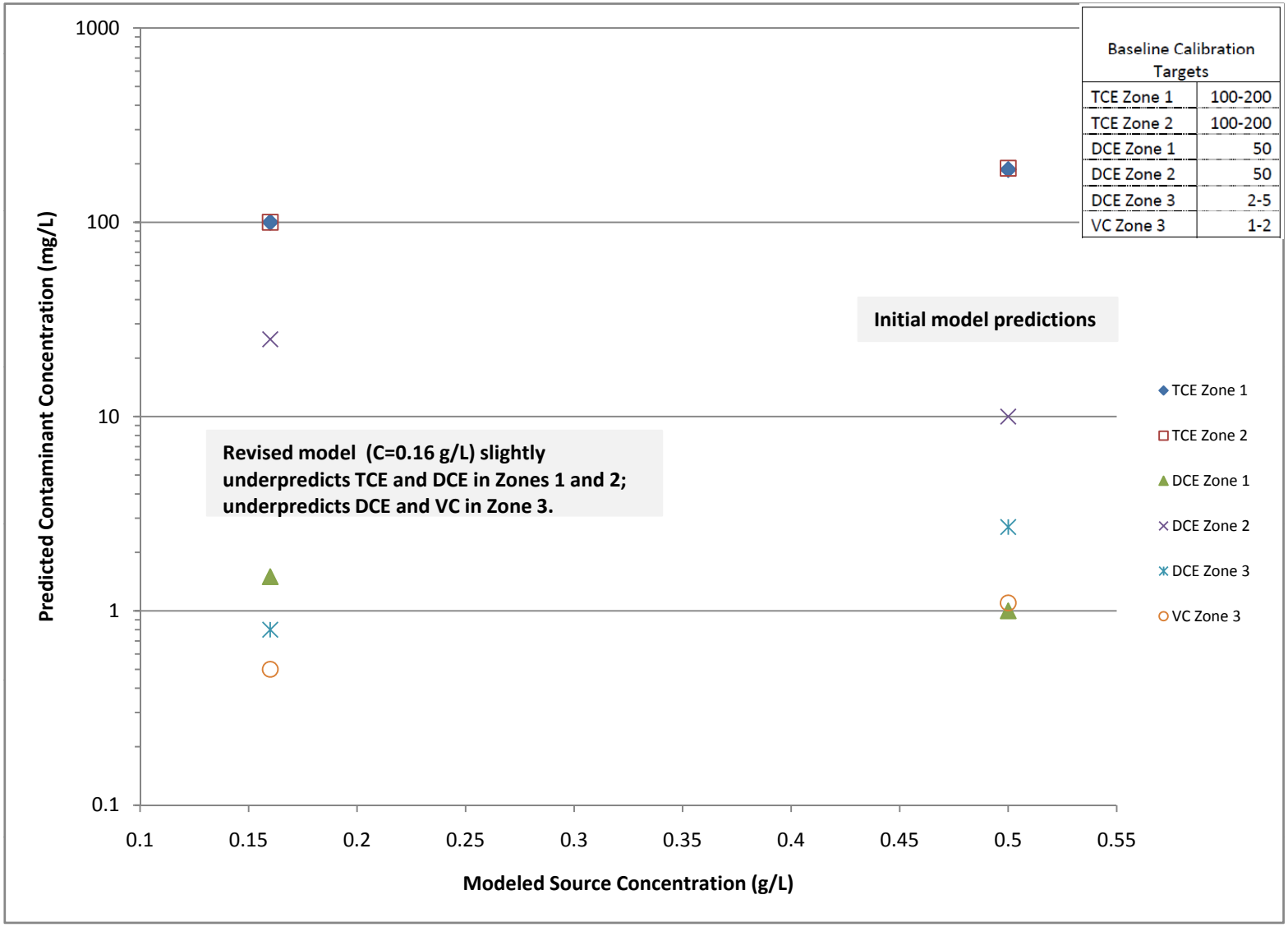

Figure 2
Sensitivity of Contaminant Concentrations to Changes in Source Concentration Two Years After Injection
Siltronic Corporation
Portland, Oregon

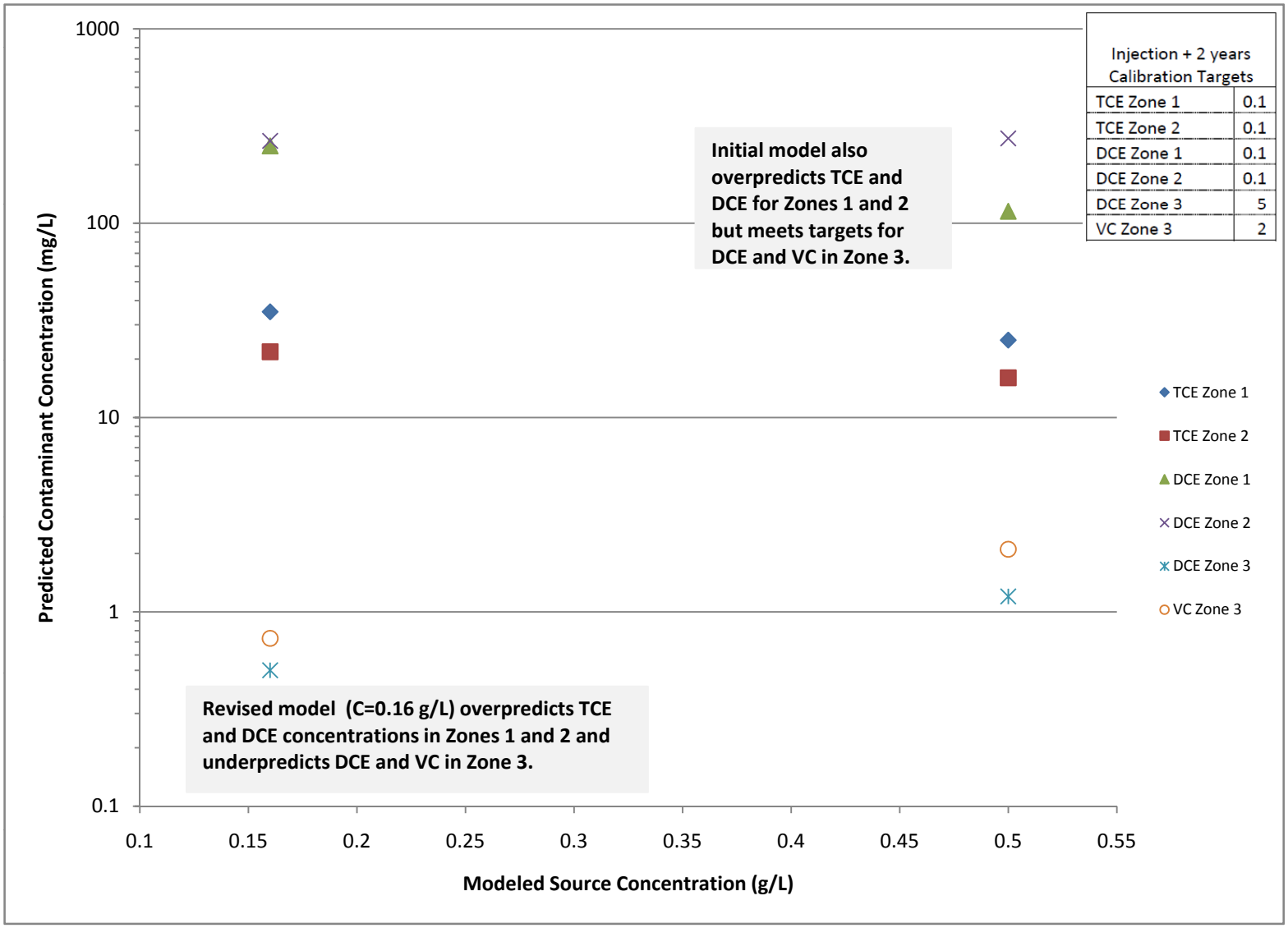

Figure 3
Sensitivity of Contaminant Concentrations to Changes in Retardation Factor at Baseline
Siltronic Corporation
Portland, Oregon

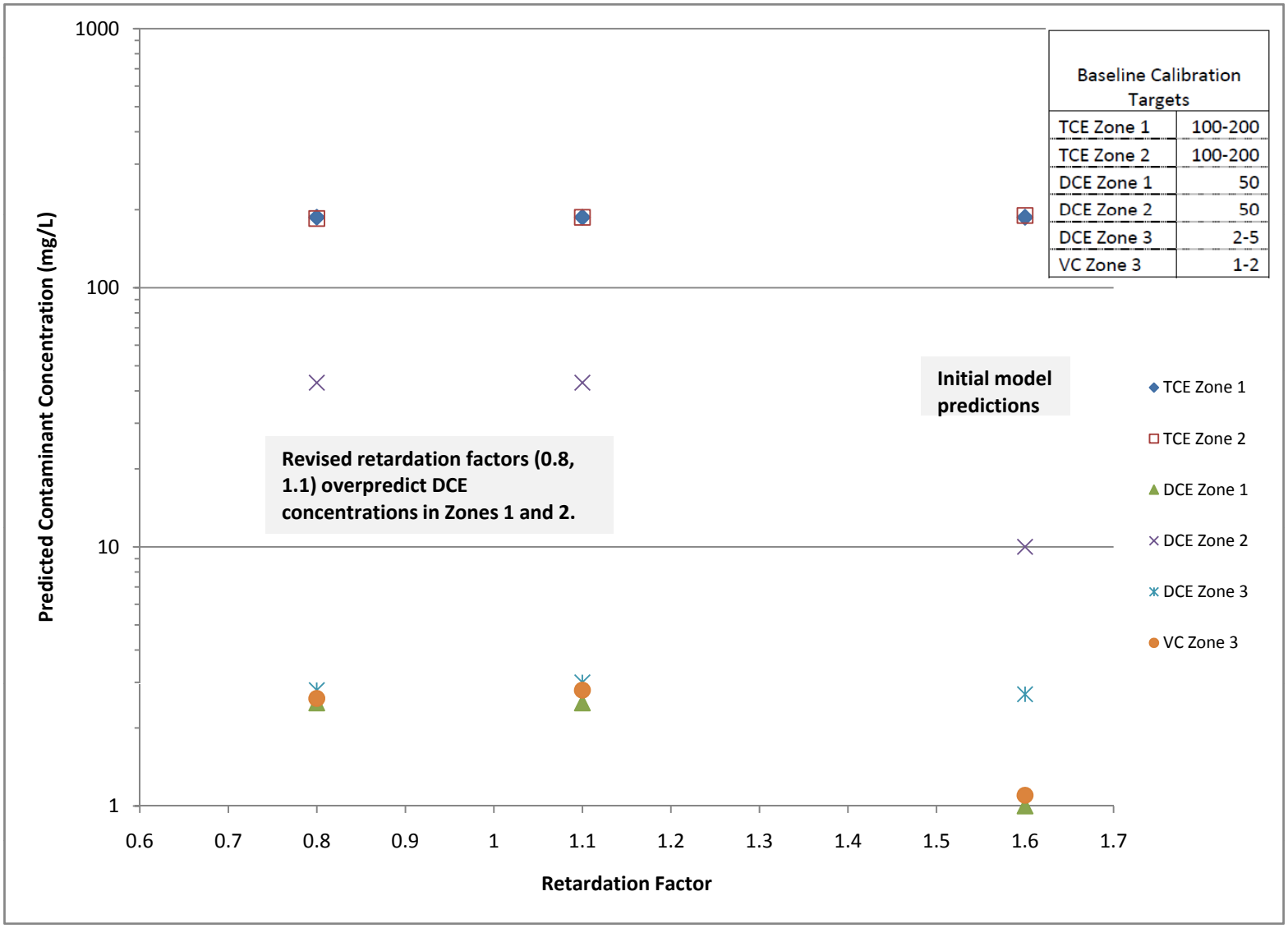

Figure 4
Sensitivity of Contaminant Concentrations to Changes in Retardation Factor at Two Years After Injection
Siltronic Corporation
Portland, Oregon

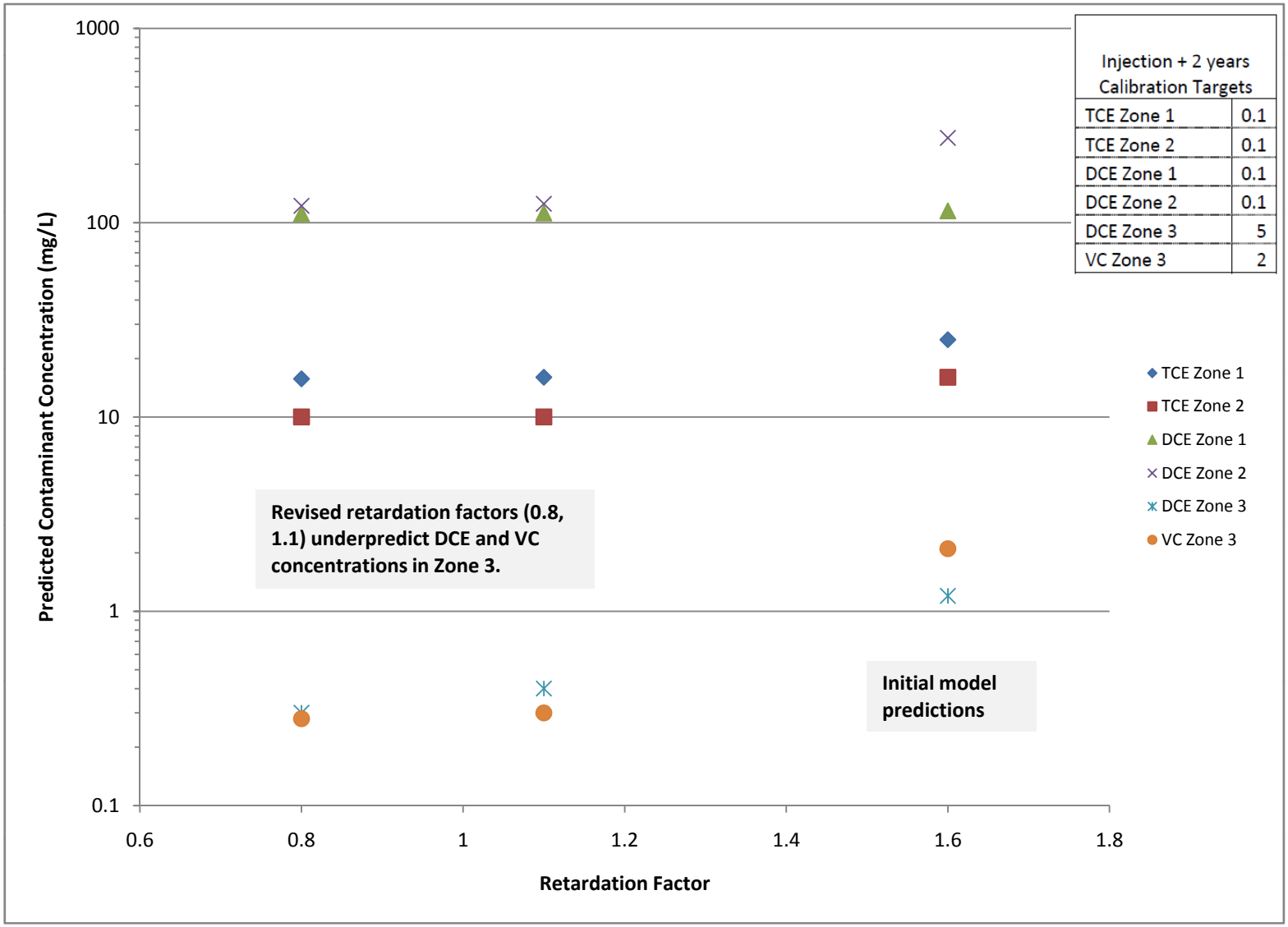

Figure 5
Sensitivity of Contaminant Concentrations to Changes in Gamma at Baseline
Siltronic Corporation
Portland, Oregon

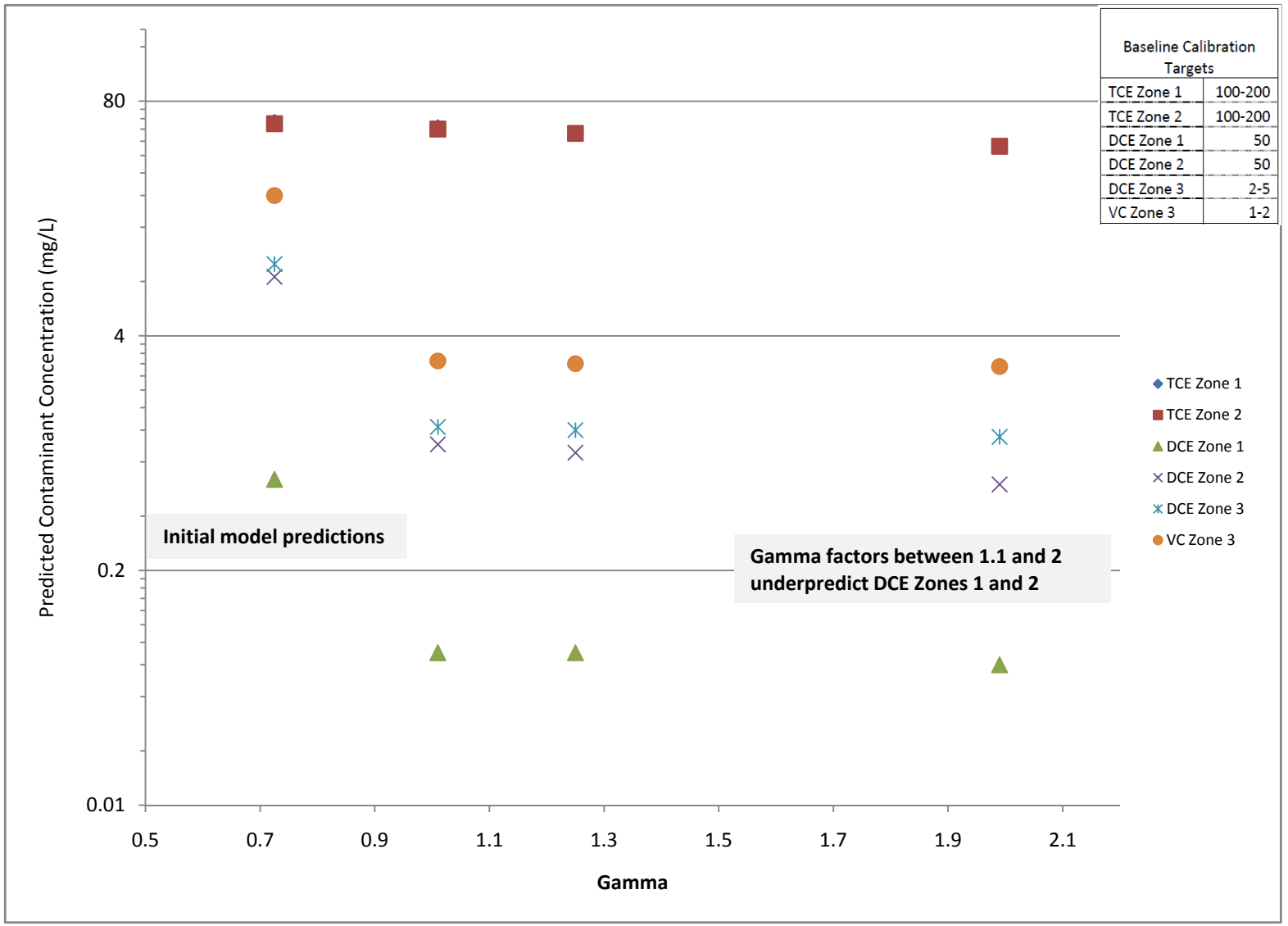

Figure 6
Sensitivity of Contaminant Concentrations to Changes in Gamma at Two Years After Injection
Siltronic Corporation
Portland, Oregon